Basic Statistical Mechanics

Randy S

Abstract Statistical mechanics is the microscopic foundation for thermodynamics. In addition to its practical applications, it plays a key role in ongoing research about the relationship between general relativity and quantum physics. This article gives a concise introduction to statistical mechanics, illustrated using a simple model that has practical applications.

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1 Introduction

In a macroscopic system made of an enormous number of molecules, we can't predict exactly what will happen to all of those molecules. Our knowledge of the initial conditions is never good enough,¹ and even if it were, solving the equations of motion in perfect detail would be too difficult.

Thankfully, we don't normally need to know exactly what will happen, and sometimes we can make useful predictions based on very little information. Suppose we have some complicated system of molecules about which we know these things:

- We know that its total energy is E.
- We know that its total volume is V.
- We know the number of mutually orthogonal states² consistent with those constraints as a function of E and V. I'll write this number as $\Omega(E, V)$.

Statistical mechanics is the art of relating $\Omega(E,V)$ to the system's thermodynamic properties. Practical applications of statistical mechanics start with our ability to determine the number $\Omega(E,V)$ from a detailed model of the system. This article introduces the basic ideas of statistical mechanics, illustrated using a simple example.

By the way, the logic can also be run in reverse: if we don't already know an appropriate detailed model, then we can use clues from thermodynamics to infer things about how the number $\Omega(E,V)$ must depend on E and V. This can give us valuable information about what a good detailed model must be like. Such clues played an important role in research about the relationship between general relativity and quantum physics, where they led to the **holographic principle**.

¹ Even a slight error in our knowledge would quickly lead to enormous errors in the prediction, because such complicated systems tend to be **chaotic**. A quantitative example is shown in https://physics.stackexchange.com/q/675735.

² The context is quantum theory, in which a state can be represented by a vector in the Hilbert space. The words **mutually orthogonal** here refer to the inner product between the vectors that represent the states. Every state vector consistent with the given constraints on E, V can be expressed as a quantum superposition of a subset of those vectors that are all orthogonal to each other in this sense.

2 When is statistical mechanics useful?

Let $\mathcal{H}(E, V)$ be the set of states that have energy $\leq E$ and volume $\leq V$, and let $\Omega(E, V)$ denote the number of states in an orthogonal basis for $\mathcal{H}(E, V)$.³ Roughly, statistical mechanics is useful when these conditions are satisfied:

- Condition 1: The number $\Omega(E, V)$ is finite.⁴
- Condition 2: Almost all of the states in $\mathcal{H}(E,V)$ "look the same" with respect to the macroscopic properties of interest. States in this majority are often called **typical**. The same condition can be expressed like this: almost all microstates give the same macrostate. A **microstates** is a complete specification of the state's microscopic details, and a **macrostate** specifies only the few macroscopic properties of interest.
- Condition 3: No matter what the microscopic details of the initial state may be, we have no reason to expect the system to remain in any specific subset of $\mathcal{H}(E, V)$.

Conditions 2 and 3 mean that we expect the system to end up spending practically all of its time in typical states, even if it started in a non-typical state. In other words, the system eventually reaches **equilibrium**. This article introduces the ideas using a relatively simple system, the **ideal gas**, as an example.

³ Mnemonic: \mathcal{H} is for *Hilbert space*, and Ω is for *orthogonal*.

⁴ Article 23206 gives a little more insight into this.

3 Entropy, temperature, and pressure

The number $\Omega(E, V)$ is finite, but it is typically enormous (section 6). Working with the natural logarithm of $\Omega(E, V)$ turns out to be convenient, so we will give this quantity a special name, **entropy**, and a special symbol:

$$S(E, V) = k \log \Omega(E, V) \tag{1}$$

where "log" is the natural logarithm function.⁵ The definition of entropy includes a factor of **Boltzmann's constant** k for convenience in practical applications, but it's nothing but a nuisance in theoretical studies, so we often use **natural units** (article 37431) in which k = 1. In this article, I'll retain the factor of k.

In statistical mechanics, everything else is derived from this one function S(E, V). To study a specific system, the first thing we need to do is obtain an explicit expression for this function. Once we have that, we can define/derive many of the system's thermodynamic properties with relative ease. In particular, the temperature T and pressure p are defined like this:

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} \qquad \qquad \frac{p}{T} \equiv \frac{\partial S}{\partial V}. \tag{2}$$

The definitions (2) might look unfamiliar, but they are simple. Most of this article is devoted to checking that they are consistent with the more familiar notions of temperature and pressure.

 $^{^5}$ Sometimes this is denoted "ln," but I prefer the notation "log" because it's easier to read. Sometimes engineers use "log" to denote the base-10 logarithm, but that's rarely used in theoretical physics, and when we do need to use it we can write it as \log_{10} instead.

4 Example: the entropy of an ideal gas

An **ideal gas** is a simple model of a gas. Despite its simplicity, it is a good approximation for some purposes. The model assumes that the system's total energy is just the sum of the kinetic energies $p^2/2m$ of the individual molecules, where p is a molecule's momentum and m is its mass. The molecules are all identical, so they all have the same mass m.

Article 23206 deduces that the number of orthogonal states of an ideal gas of N identical molecules is 6

$$\Omega(E, V) \propto \left(\frac{m}{\hbar^2} E\right)^{DN/2} V^N$$
(3)

where \hbar is Planck's constant and D is the number of spatial dimensions.⁷ The derivation of (3) uses quantum physics (article 23206), and the presence of \hbar is a symptom of this. The proportionality factor depends on the number of molecules N, but that won't matter in this article because we will regard N as a fixed quantity (no molecules enter or leave the given volume).

Use equations (1), (3), and the properties of the function $\log x$ to get

$$S(E, V) = \text{constant} + \frac{DN}{2}k \log E + Nk \log V.$$
 (4)

This is the entropy of an ideal gas of N molecules. The constant (E- and V-independent) term comes from the unwritten proportionality factor in equation (3) and from the factor m/\hbar^2 .

⁶ A molecule with angular momentum L is a **fermion** if L is an odd integer multiple of $\hbar/2$ and is a **boson** if L is an even integer multiple of $\hbar/2$. Equation (3) assumes that E, V are large enough (or that N is small enough) so that the difference between the fermion and boson cases is insignificant (article 23206). This is a **classical** ideal gas, except for the N-dependent proportionality factor that I'm not showing here anyway.

⁷ Even though D=3 in the real world, the math is just as easy for D-dimensional space, so we might as well keep it general.

5 Temperature and pressure of an ideal gas

The temperature and pressure of an ideal gas are easily computed from the definitions (2), using equation (4) for the entropy. For the temperature T, the definition (2) gives

$$kT = \frac{2E}{DN}. (5)$$

This says that temperature of an ideal gas is proportional to the average energy per molecule – specifically the average *kinetic* energy per molecule, because all of the energy of an ideal gas is kinetic. This is consistent with the more familiar physical concept of temperature.⁸ Section 11 shows another check that the definition (2) is consistent with our usual concept of temperature.

For the pressure p, the definition (2) gives

$$pV = NkT. (6)$$

This is called the **equation of state** for an ideal gas.

⁸ In most models of interest, the temperature is an increasing function of E, but exceptions do exist, like the one described on page 105 in Reif (1965).

6 Some numbers for perspective

Equations like (3) and (4) are easy to write, but they represent numbers of enormous magnitude. As an example, consider one gram of nitrogen gas at room temperature and standard atmospheric pressure.⁹ The number of molecules in one gram of nitrogen is $N \sim 2 \times 10^{22}$. (The notation " \sim " indicates a very rough approximation.) Section 5 showed how to calculate V and E from this information. Here are the results: The volume is $V \sim 1$ liter, and the energy¹⁰ is $E \sim 100$ joules. Use these quantities to get

$$\left(\frac{m}{\hbar^2}E\right)^{3/2}V \sim 10^{68}.$$

After restoring the N-dependent factor that was omitted in equation equation (3), the number of orthogonal states is

$$\Omega(E,V) \sim \frac{1}{N!} \left(\left(\frac{m}{\hbar^2} E \right)^{3/2} V \right)^N.$$

With the help of **Stirling's approximation** for N!, we can write this as

$$\Omega(E, V) \sim N^{-1/2} \left(\frac{e}{N} \left(\frac{m}{\hbar^2} E \right)^{3/2} V \right)^N$$

 $\sim 10^{-11} \times (5 \times 10^{46})^N$

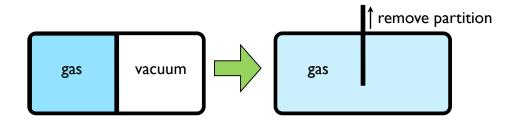
That's a big number. The number of digits we would need just to write the number $\Omega(E, V)$ in base 10 is even larger than the number of molecules in the gas! A number like $10^{1000000}$ is tiny compared to this.

Most of the molecules in the atmosphere are nitrogen molecules (N₂). One mole ($\approx 6 \times 10^{23}$ molecules) of N₂ has a mass of approximately 28 grams.

¹⁰ This value of E represents the sum of the molecules' kinetic energies, as assumed by the ideal gas model. It does not include the energy mc^2 that is stored in the mass of each molecule, which would only be relevant in extreme circumstances where that energy could be accessed and converted to other forms.

7 Typical states and volume, part 1

Consider an airtight cylinder with two chambers separated from each other by a removable partition, as illustrated here:



Initially, one chamber is filled with gas and the other chamber is empty (vacuum). What happens when the partition is removed? Let V be the total volume inside the cylinder. When the partition is removed, we expect the gas to quickly fill the whole volume V with a (lower) uniform density, as shown in the diagram.

Why do we expect the gas to fill the volume V? The set $\mathcal{H}(E,V)$ of allowed states includes states in which the density is far from uniform, but:

- Almost all of the states in $\mathcal{H}(E,V)$ have practically uniform density. In other words, states with uniform density are typical. The next section checks this for the ideal gas model.
- We don't expect the gas to favor any special subset of $\mathcal{H}(E,V)$.

These are conditions 2 and 3 in section 2, and this is why we expect the density to end up being practically uniform.

By the way, just like states with practically uniform density are typical, states with a particular distribution of molecular velocities are also typical. For a classical ideal gas (footnote 6), the typical distribution of velocities is called the **Maxwell-Boltzmann distribution**.

¹¹ Suppose that the total energy E of the gas does not change, which amounts to assuming that the cylinder is perfectly thermally insulated. The total number N of molecules does not change because the cylinder is airtight.

8 Typical states and volume, part 2

The previous section asserted that states with practically uniform density are typical. To check this, write the number of orthogonal states as $\Omega(E, V, N)$ to indicate the number N of molecules explicitly, and consider the product

$$f(\nu) \equiv \Omega(\epsilon, \nu, n)\Omega(E - \epsilon, V - \nu, N - n), \tag{7}$$

which is the number of states for which n of the molecules occupy a part of the cylinder with volume ν and the remaining molecules occupy the remaining volume, 12 and a given distribution of energy. According to equation (3), the number (7) is proportional to

$$f(\nu) \propto \nu^n (V - \nu)^{N-n} \tag{8}$$

with a ν -independent overall factor. For a given value of n, the value of ν that maximizes this quantity is the one that satisfies $df/d\nu = 0$. This condition is equivalent to $d \log f/d\nu = 0$, which in turn is equivalent to

$$\frac{n}{\nu} = \frac{N - n}{V - \nu}.\tag{9}$$

This says that the number (7) is maximized when the densities are equal to each other, in which case they are both equal to N/V.

Now consider all possible values of ν . Almost all states in this ensemble satisfy the condition $n/\nu = N/V$ almost exactly. To see this, write the function (8) as

$$f(\nu) \propto \left(\nu^r (V - \nu)^{1-r}\right)^N \tag{10}$$

with $r \equiv n/N$. We already determined that the function $\nu^r(V-\nu)^{1-r}$ is maximized by $\nu = rV$, and in (10) this function is raised to the Nth power with $N \sim 10^{23}$. That amplifies the height and narrowness of the peak to an extreme degree (figures 1 and 2 show the trend), so the number of states with other values of ν is negligible compared to those with v very close to V/N.

¹² For the quantum version of an ideal gas, we don't need to (and can't) specify *which* molecules, because observables are tied to regions of space, not to individual molecules. This is traditionally expressed by saying that the molecules are **indistinguishable**.

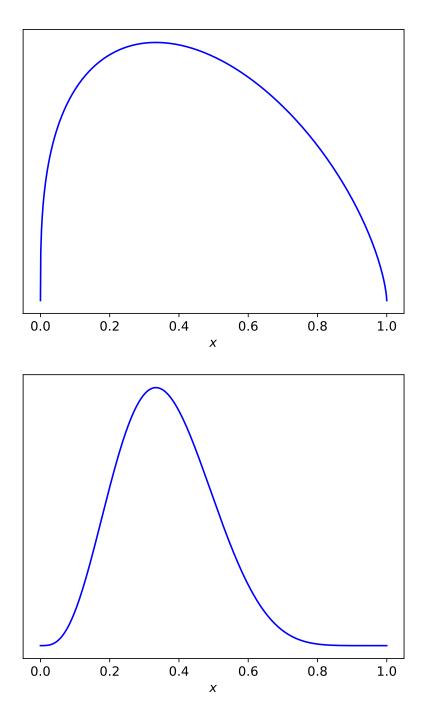


Figure 1 – Graphs of the function $(\omega(x))^N$ with N=1 (top) and N=10 (bottom), where $\omega(x)=x^r(1-x)^{1-r}$ and r=1/3. (Compare to equation (10) with $x\equiv\nu/V$.) Figure 2 shows the graphs for N=100 and N=1000.

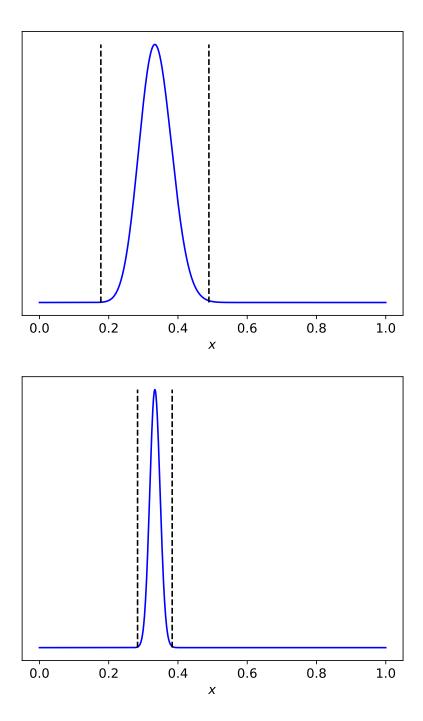
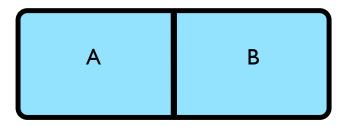


Figure 2 – Graphs of the function $(\omega(x))^N$ with N=100 (top) and N=1000 (bottom), where $\omega(x)=x^r(1-x)^{1-r}$ and r=1/3. The vertical dashed lines indicate the range of x-values that contains 99.9% of the area under the curve.

9 Typical states and energy, part 1

Here's another example of condition 2 in section 2. Consider a system composed of two subsystems whose individual volumes are fixed but that can exchange energy with each other. To be specific, consider a cylinder with two gas-filled chambers A and B separated by a partition. The position of the partition is fixed, so the volumes on each side are fixed, but the partition conducts heat so that the gas on one side can exchange energy with the gas on the other side:



The number of orthogonal states of the combined system is

$$f(\epsilon) = \Omega_A(\epsilon)\Omega_B(E - \epsilon) \tag{11}$$

where E is the total energy of the combined system and ϵ is the energy of subsystem A. The volume-dependence is not indicated, because the volumes are all fixed. The subscripts on Ω_A , Ω_B allow for the fact that the two sides could have different volumes, different densities, different numbers of molecules, and even different types of molecules.

The next section shows that for an ideal gas, if the number of molecules is sufficiently large, then almost all of the states of the combined system have almost exactly the same value of ϵ . This is another example of condition 2 in section 2.

10 Typical states and energy, part 2

Consider an ideal gas. We can use the same approach as in section 8, but now focusing on the energy instead of on the volume. Let N be the total number of molecules, so that the numbers of molecules in subsystems A and B are rN and (1-r)N for some 0 < r < 1. Using equation (3) in (11) gives

$$f(\epsilon) \propto \left(\epsilon^r \times (E - \epsilon)^{(1-r)}\right)^{ND/2}$$
.

Using the same technique that led to equation (9), we find that the quantity

$$\epsilon^r \times (E - \epsilon)^{(1-r)} \tag{12}$$

has a maximum at the value of ϵ that satisfies

$$\frac{r}{\epsilon} = \frac{1 - r}{E - \epsilon},\tag{13}$$

namely $\epsilon = rE$. After raising (12) to a large power, like $DN/2 \sim 10^{23}$, the resulting function is almost entirely concentrated within a very narrow range of ϵ -values about rE. This shows that the number of states with other values of ϵ is negligible compoared to those with ϵ very close to rE.

11 Temperature and equilibrium

Our usual intuition about temperature says that two systems that can exchange energy with each other should end up having the same temperature. Let's see how to derive this property from the entropy-based definition of temperature in equation (2).

As in sections 9-10, consider a system composed of two subsystems whose individual volumes are both fixed, but their individual energies are not: they can exchange energy, so that only the total energy is fixed. Suppose that condition 2 in section 2 is satisfied, as demonstrated in the previous section. Almost all of the microstates have almost exactly one special value of ϵ , namely the one that maximizes the product (11). From this we can infer that the number of microstates with total energy E is

$$\Omega(E) \propto \Omega_A(\epsilon)\Omega_B(E-\epsilon)$$

to a good approximation, so the entropy is

$$S(E) \approx S_A(\epsilon) + S_B(E - \epsilon) + \text{constant}$$

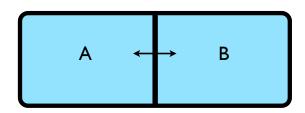
to a good approximation. By definition, the typical value ϵ is the one that maximizes the summand in (11), so it satisfies the maximization condition

$$\frac{d}{d\epsilon} \Big(S_A(\epsilon) + S_B(E - \epsilon) \Big) = 0.$$

According to the entropy-based definition of temperature, the first of equations (2), this implies $T_A = T_B$. In other words, assuming that condition 2 in section 2 is satisfied (as shown in the previous section), for practically all states of the combined system, the temperatures of the two subsystems are equal to each other. This is consistent with the more familiar concept of temperature.

12 Pressure and equilibrium

Consider two subsystems that can exchange both energy and volume with each other. To be specific, consider two gas-filled chambers separated from each other by a partition that conducts heat (so the gases can exchange energy) and that is freely movable (so the gases can exchange volume), as depicted here:



Our usual intuition about pressure says that in this situation, the two subsystems should end up having the same temperature and the same pressure.

To derive this from the entropy-based definitions (2), let N_A and N_B denote the numbers of molecules in A and B. We're assuming that the partition is impermeable, so these numbers are fixed. We can use the same kind of reasoning as in sections 8 and 10, now applied to the product

$$\Omega_A(\epsilon, \nu)\Omega_B(E - \epsilon, V - \nu).$$
 (14)

For an ideal gas, this is maximized by

$$\epsilon = rE$$
 $\nu = rV$

with

$$r = \frac{N_A}{N_A + N_B}.$$

If the number of molecules is sufficiently large, then the function (14) is almost entirely concentrated within a very narrow range about these special values of ϵ and ν . Just like in section 11, this shows that the two subsystems have practically equal temperatures and pressures for practically all states of the combined system.

This is an example of condition 2 in section 2. Combining this with condition 3 in section 2, we expect that the two subsystems will end up having the same temperature and the same pressure. This is consistent with the familiar concept of pressure.

In this example, we allowed the subsystems to exchange both energy and volume (instead of only volume) because:

- The definition of pressure in equation (2) also involves the temperature, so if only volume-exchange were allowed, then both subsystems would end up having the same p/T, but not necessarily the same T and therefore not necessarily the same p.
- In contrast to keeping the volumes of A and B fixed, which we can do just by making the partition non-movable, finding a way to keep the energies of A and B fixed (while still allowing them to exchange volume) is trickier. For an ideal gas, equation (5) says that we could do this by keeping the their temperatures fixed, but for non-ideal gases the temperature may depend on both E and V, not just on E.

13 The first law of thermodynamics

If the energy and/or volume are changed by small amounts dE and dV, respectively, then the corresponding change in entropy is

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV. \tag{15}$$

This is a mathematical identity. It relies only on the fact that S is a smooth function of E and V, and on the assumption that E and V are the only variable inputs to S. (Equation (15) assumes that other inputs, like N, are fixed.) According to the definitions (2), the same identity may also be written like this:

$$T dS = dE + p dV. (16)$$

This is called the **First Law of Thermodynamics**. It applies whenever the changes are small.

14 Heat and work

The first law (16) includes these special cases:

- If dV = 0, then dE = T dS. This way of exchanging energy is called **heat**.
- If dS = 0, then dE = -p dV. This way of exchanging energy is called **work**.

More generally, though, T dS isn't always what we normally call heat, and p dV isn't always what we normally call work. To see this, consider a configuration like the one depicted in section 7, but with lots of very closely spaced partitions instead of only one, and with no gas between the partitions. Suppose that the system is completely self-contained, with no outside world to interact with, so dE = 0. Let V be the volume occupied by the gas.¹³ Removing the innermost partition (the only one in contact with the gas) changes the volume by a very small amount dV > 0 if the distance to the next partition is very small. Equation (4) says that this also gives dS > 0. At least on paper, we can make these changes as small as we like, so we can use the first law (16). However:

- Even though p dV > 0, we would not normally say that any work is being done by (or on) the gas in this process.
- Even though T dS > 0 we would not normally say that any *heat* is going into the gas in this process.

This shows that T dS isn't always what we normally call heat, and p dV isn't always what we normally call work. The beginning of this section defined heat and work only for dV = 0 and dS = 0, respectively. They can be defined more generally when we have a clear separation of different scales (microscopic and macroscopic), which is often the case in practice, but I won't try to formalize that here. Instead, I'll avoid using the terms heat and work at all, except when dV = 0 and dS = 0 (respectively) where their definitions are straightforward.

 $^{^{13}}$ This is different than section 7, where V included the part of the cylinder that was initially *not* occupied by gas.

15 The second law of thermodynamics

The **second law of thermodynamics** says that the entropy of an isolated system does not decrease. If we consider the entropy S(E, V) to be a function of the constraints that we *impose* on E and V, then the entropy of an isolated system cannot change at all – because the system wouldn't really be isolated if an external agent changed the imposed values of E and V. However, if we consider the entropy S(E, V) to be a function of *known* constraints on E and V, then the entropy can increase with time.

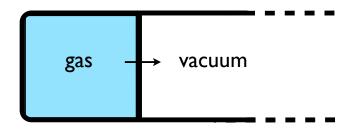
To illustrate this, consider the case depicted in section 7. Immediately after the partition is removed, the *imposed* constraint on the volume of the gas is the total volume of the cylinder, but the volume that the gas is known to occupy is smaller, because the molecules don't move infinitely fast, so we know that the occupied volume grows at a finite rate. If V denotes the smallest volume in which we know the gas must still be contained because we know something about how fast the molecules move, then the entropy S(E, V) increases at a finite rate while the gas is expanding to fill the cylinder. This illustrates the sense in which the entropy of an isolated system can increase with time.

More generally, the second law is really just a restatement of condition 3 in section 2. Those conditions say that the system should eventually end up spending practically all of its time in typical states, but they don't prevent the system from starting in a very non-typical state, like the gas in section 7 immediately after the partition is removed. If the system starts in a non-typical state, then reaching equilibrium (the condition of spending practically all of its remaining time in typical states) takes time. If we know enough about the system's dynamics, then we may be able to say something about how its macroscopic properties will change with time. Condition 3 says that the change will always be in the direction of increasing entropy, which is the second law of thermodynamics. Of course, this is only a statement about our incomplete knowledge of the system, but this incomplete knowledge is often enough to make *very* confident preditions, as emphasized at the end of sections 8 and 10.

16 Relating pressure to force

The everyday concept of pressure is defined as a force per unit area. Is that consistent with the entropy-based definition of pressure given by equations (2)?

To check this, consider a cylinder with a partition that can slide along the length of the cylinder without friction. Suppose that one side is filled with gas and the other side is empty (vacuum), as depicted here:



Suppose that:

- The gas and the partition do not exchange energy with the fixed walls of the cylinder.
- The gas can exchange energy with the partition, but only through the motion of the partition's center-of-mass.

The system consisting of the gas and the partition's center-of-mass is **isolated**: it is neither influencing nor being influenced by anything else. The total energy of an isolated system is conserved, so if E is the energy in the gas and \tilde{E} is the kinetic energy of the partition's center-of-mass motion, then $E + \tilde{E}$ is constant in time. Each collision of a gas molecule with the partition transfers some energy from E to \tilde{E} (or conversely, depending on which direction the partition is moving), but their sum remains constant.

Suppose that the partition moves slowly enough so that the gas is always in equilibrium – that is, practically always in states that are typical for the current volume – so that the distinction between the imposed volume and the known volume

(section 15) does not matter. Even though E and V are both changing, the entropy S(E,V) of the gas is constant to an excellent approximation. That's because the equations of motion governing an *isolated* quantum system are **unitary**, which means that initially-orthogonal states remain orthogonal as time passes. ¹⁴ Entropy quantifies the number of orthogonal states, so the total entropy of the system cannot change. This total entropy includes the entropy of the gas and of the partition's center-of-mass states, but the latter is negligible because the partition is treated as one big elementary object compared to $N \sim 10^{23}$ molecules in the gas. Therefore, the entropy S(E,V) of the gas itself is constant to an excellent approximation.

We can choose a brief interval of time and apply first law (16) to that interval, because the changes during that interval are small. Since dS = 0 as explained above, the first law gives dE + p dV = 0, which can also be written p = -dE/dV. We can write the change in volume as dV = A dx, where A is the partition's area and dx is the change in its position along the length of the cylinder. This gives

$$p = -\frac{dE/dx}{A}.$$

The quantity dE in the numerator is the change in the energy E of the gas. If \tilde{E} denotes the kinetic energy of the partition's center-of-mass motion, then $E + \tilde{E}$ is constant because we assumed that no energy is lost into the microscopic details of the walls or partition. This implies

$$p = \frac{d\tilde{E}/dx}{A}.$$

The quantity F defined by $d\tilde{E} = F dx$ is the force applied to the partition, because work = force × distance. Altogether, this gives p = F/A. The p in this equation is the entropy-based definition of pressure (equations (2)), so this result confirms that the entropy-based definition of pressure is consistent with the everyday concept of pressure: force per unit area.

¹⁴ Unitary is a stronger condition than reversible.

17 References

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